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(54) Title: PROCESS CATALYSED BY BIS-TRIFLIMIDE COMPOUNDS

(57) Abstract: A process for carrying out a chemical reaction which is catalysed by one or more metal or hydrogen fluoroalkyl-sulfonylated compound which process comprises carrying out said reaction in the presence of an ionic liquid or in solvent-free conditions.

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12 **PROCESS CATALYSED BY BIS-TRIFLIMIDE COMPOUNDS**

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14 The present invention relates to a process for
15 carrying out a chemical reaction which is catalysed
16 by bis-triflimide and related bis-trifilimide
17 compounds. More specifically, the present invention
18 relates a process for carrying out such chemical
19 reactions in the presence of an ionic liquid or in
20 solvent-free conditions.

21

22 The catalysis of chemical reactions is of major
23 importance in chemistry. The salts of certain
24 metals are known to act as Lewis acids (electron
25 pair acceptors), which interact with the reactants
26 (and products) of a reaction, producing a reaction
27 rate enhancement and/or selectivity enhancement.
28 Also salts of metals which can exist in variable
29 oxidation states (such as transition metals) are
30 known to catalyse chemical reactions such as

1 Friedel-Crafts, oxidation, reduction, Diels-Alder,
2 isomerisation, coupling, addition and elimination
3 reactions. The Friedel-Crafts reaction is often
4 used to functionalise aromatic rings. The reaction
5 involves the interaction of an acylating or
6 alkylating agent such as benzoyl chloride or benzyl
7 chloride with an aromatic compound such as benzene
8 to give the products, in this case, benzophenone and
9 diphenylmethane. The reaction requires a Lewis acid
10 catalyst such as aluminium(III) chloride. The
11 reaction suffers from a major disadvantage in that,
12 particularly with acylation reactions, at least one
13 molar equivalent of Lewis acid catalyst is needed.
14 The work-up of these reactions results in the
15 destruction of the catalyst and can produce
16 considerable amounts of acidic aqueous waste. There
17 is a need for an improved catalyst system which
18 requires less catalyst, produces less waste and
19 allows for the catalyst to be reused and recycled.

20

21 Metal bis-triflimides are known as catalysts for
22 some reactions. Examples include polymerisation of
23 styrene with titanium (or zirconium) bis-triflimides
24 in the solvent toluene. Magnesium bis-triflimide
25 has been used for the reaction of silyl-enol ethers
26 or silyl-ketene acetals with allylic or benzylic
27 acetates in the solvent dichloromethane. Scandium
28 bis-triflimide has been used as a catalyst for the
29 formation of acetals and ketals from carbonyl
30 compounds (or enol ethers) in the solvent

1 dichloromethane. Aluminium, ytterbium and titanium
2 bis-triflimides have been used in the reaction of
3 acetic anhydride with anisole or diphenyl ether to
4 give acetyl anisole or 4-phenoxyacetophenone
5 respectively. These reactions are carried out in
6 the dangerous and explosive solvent, nitromethane.
7 Such a procedure is of very limited benefit as
8 aromatics less reactive than anisole would require
9 elevated reaction temperatures and can only be
10 carried out on a small scale due to the inherent
11 explosion risk. There is therefore a need for a
12 reaction system that does not require the use of
13 explosive solvents such as nitromethane or toxic
14 solvents such as toluene or dichloromethane.

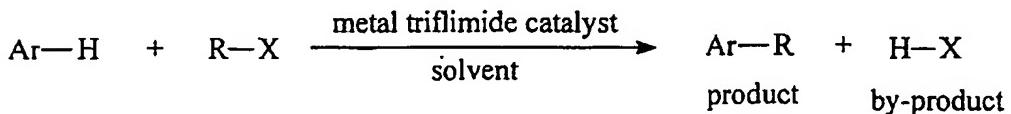
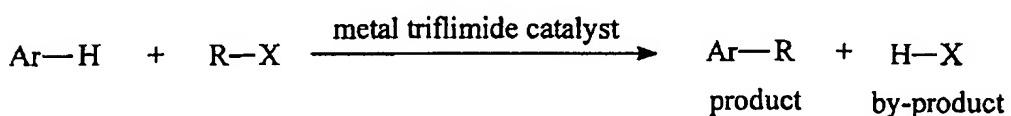
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16 The present invention solves the problems of the
17 prior art by providing a process for carrying out a
18 chemical reaction which is catalysed by one or more
19 metal or hydrogen fluoralkylsulfonated compound
20 which process comprises carrying out said reaction
21 in the presence of an ionic liquid or in solvent-
22 free conditions.

23

24 Suitably the chemical reaction is an aromatic
25 electrophilic substitution reaction such as the
26 reaction of an aromatic compound and an alkylating,
27 acylating or sulfonating agent to give an
28 arylalkane, aryl ketone or sulfone. The reaction
29 may be a Friedel-Crafts acylation, Friedel-Crafts
30 alkylation or a sulfonylation. The reaction may be

1 the reaction of acid halides, anhydrides or
 2 carboxylic acids with aromatic compounds to give an
 3 aryl ketone. The reaction can be a reaction of
 4 sulfonyl halides, sulfonic anhydrides or sulfonic
 5 acids with aromatic compounds to give a sulfone.
 6 The reaction may be a reaction of alkenes with
 7 aromatic compounds to give aryl alkanes. The
 8 reaction may also be a bis-triflimide compound
 9 catalysed or promoted isomerisation, polymerisation
 10 or rearrangement of chemical compounds or molecules.
 11 The reaction may be a rearrangement of esters of
 12 phenols to acyl phenols (Fries rearrangement). The
 13 reaction may be a dimerisation (or oligomerisation
 14 or polymerisation) of alkenes to give dimerised
 15 alkenes (or oligomerised or polymerised alkenes).
 16 The reaction can be the migration or isomerisation
 17 of carbon-carbon double bonds in unsaturated
 18 compounds. The reaction can be an hydration,
 19 nitration, carbon-carbon bond forming reaction,
 20 halogenation, oxidation or reduction reaction. A
 21 general reaction scheme for the reactions catalysed
 22 using metal bis-triflimides is shown below:
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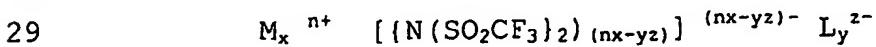
1 where Ar = aromatic group, R = alkyl, acyl,
2 alkylsulfonyl, arylsulfonyl. X = Cl, OH, Br, I, F,
3 OR, SH, NR₂, OSO₂R, O₂CR or other leaving group.

4

5 By metal or hydrogen fluoroalkylsulfonylated
6 compound is meant a compound derived from a metal or
7 hydrogen cation and [N(SO₂C_xF_(2x+1))₂]⁻ anion. For
8 example, the catalyst can be any compound containing
9 a metal and a fluorinated-alkylsulfonylated anion
10 (preferably a fluorinated-alkylsulfonylamine anion).

11 The one or more metal or hydrogen
12 fluoroalkylsulfonylated compound is preferably a
13 metal or hydrogen bistriflimide. By bis-triflimide
14 compound is meant any compound which comprises the
15 ion [N(SO₂CF₃)₂]⁻. This ion is commonly known by the
16 following names: triflimide,
17 bis(trifluoromethanesulfonyl)amide, bis-
18 trifluoromethanesulfonimide,
19 bis(trifluoromethanesulfonyl)imide,
20 trifluoromethanesulfonimide. In this document, the
21 term bis-triflimide will be used as the name for the
22 [N(SO₂CF₃)₂]⁻ ion. Also, the abbreviation [NTf₂] is
23 sometimes used to represent the [N(SO₂CF₃)₂]⁻ ion.
24 Preferably the bis-triflimide compound is a metal
25 bis-triflimide catalyst or hydrogen bis-triflimide
26 HN(SO₂CF₃)₂. The formula of the hydrogen and metal
27 bistriflimide catalyst is

28



30

1 where M is a hydrogen or a metal;
2 L is a negative or neutral ligand;
3 n is 2,3,4,5,6,7 or 8 ;
4 x is greater than or equal to 1
5 y is 0,1,2,3,4,5,6,7or 8; and
6 z is 0, 1,2,3 or 4.

7

8 M may represent more than one type of metal ion. M
9 is preferably a metal selected from the metals in
10 groups 1 to 16 of the periodic table and the
11 lanthanides and the actinides. By group 8 is meant
12 the group containing Fe, Ru, Os, Hs, by group 9 is
13 meant the group containing Co, Rh, Ir, Mt, etc. L
14 may be selected from oxos (such as VO^{2+}), phosphines
15 (such as triphenylphosphine), water, halides or
16 ketones. The ligand may originate from a solvent,
17 reagent or by-product in the reaction mixture for
18 making the catalyst or the reaction mixture in which
19 the catalyst is used.

20

21 The metal or metals may possess one or more neutral
22 or negative ligands (such as triphenylphosphine or
23 oxo (such as in VO_2^+)) or any other ligand such as as
24 oxo, phosphines, water, halide or ketones.
25 Preferably the metal or metals are preferably, but
26 not exclusively, a transition metal, lanthanide or
27 actinide, group 2 (Be, Mg, Ca, Sr, Ba), Group 11
28 (Cu, Ag, Au), Group 12 (Zn, Cd, Hg) Group 13 (B, Al,
29 Ga, In, Tl), Group 14 (Si, Ge, Sn, Pb), Group 15 (P,
30 As, Sb, Bi), Group 16 (S, Se, Te, Po). Preferably

1 the metal or metals are preferably, but not
2 exclusively in the +2 oxidation state (eg Co^{2+}), in
3 the +3 oxidation state (eg Al^{3+}) or in the +4
4 oxidation state (eg Ce^{4+}). Cationic species
5 containing charged ligands could also be used (eg
6 UO_2^{2+} , VO^{2+}). Monovalent, pentavalent, heptavalent and
7 hexavalent cationic species may also be used.
8 Particularly preferred metal bis-triflimide compounds
9 which have been prepared and isolated for use in the
10 catalytic reactions of the present invention include
11 magnesium bis-triflimide, calcium bis-triflimide,
12 strontium bis-triflimide, barium bis-triflimide,
13 aluminium bis-triflimide, gallium bis-triflimide,
14 indium bis-triflimide, scandium bis-triflimide,
15 yttrium bis-triflimide, lanthanum bis-triflimide,
16 cerium bis-triflimide, ytterbium bis-triflimide,
17 chromium bis-triflimide, manganese bis-triflimide,
18 iron bis-triflimide, cobalt bis-triflimide, nickel
19 bis-triflimide, copper bis-triflimide, zinc bis-
20 triflimide, silver bis-triflimide, cadmium bis-
21 triflimide, tin bis-triflimide, lead bis-triflimide,
22 and bismuth bis-triflimide.

23

24 Typically, the reactions of the present invention
25 require an amount of bis-triflimide compound is
26 between 0.000001 and 1000 mol %, typically this is
27 between 0.1 and 10 mol %, preferably it is between
28 0.5 and 5 mol % and more preferably this is between
29 between 0.5 and 2 mol %.

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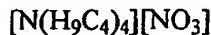
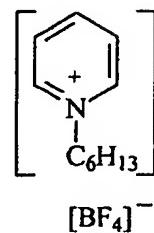
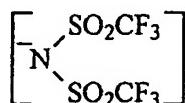
1 The process may involve the addition of the bis-
2 triflimide catalyst to the reactants, e.g. the
3 addition of 1 mol % of Zn(NTf₂)₂ to a mixture of an
4 alkylating agent or acylating agent or sulfonylating
5 agent and aromatic compound. This can be carried
6 out either in the presence of an ionic liquid or in
7 solvent-free conditions. When carried out in the
8 presence of an ionic liquid, the catalyst may be
9 dissolved or suspended in an ionic liquid. An ionic
10 liquid is a molten salt that is in a liquid state at
11 the reaction temperature and usually (but not
12 essentially) molten at or near room temperature,
13 i.e., 20 °C. When carried out in solvent-free
14 conditions, the catalyst may be soluble, or
15 partially soluble, in the reactants or products
16 (these can act as both solvent and reagent). The
17 products can be separated from the catalyst at the
18 end of the reaction by distillation or solvent
19 extraction with a solvent that the catalyst is
20 insoluble in (for example cyclohexane).

21

22 An ionic liquid is a molten salt or mixture of salts
23 that is in the liquid state at the temperature of
24 the reaction. The ionic liquids (if used) are
25 preferably molten salts that are in the liquid state
26 at ambient temperatures, and preferentially dissolve
27 the catalyst when contacted with the reagents.
28 Preferably the catalyst is soluble in the ionic
29 liquid to a much greater extent than the products
30 and/or reactants during the separation of the

1 catalyst from the products/reactants. The ionic
2 liquid consists of two components, which are a
3 positively charged cation and a negatively charged
4 anion. Preferably the cation is an organic cation
5 and the anion is an organic or inorganic anion.
6 That cation for the process is preferably a 1-
7 alkylpyridinium (such as 1-hexylpyridinium) or 1,3-
8 dialkylimidazolium cation such as 1-butyl-3-
9 methylimidazolium [bmim] or 1-ethyl-3-
10 methylimidazolium [emim]. Other cations for this
11 process are other alkyl- or poly-alkylpyridinium,
12 alkyl or poly-alkylimidazolium, alkyl or poly-
13 alkylpyrazolium, alkyl or poly-alkyl ammonium, alkyl
14 or poly-alkyl phosphonium, other ammonium,
15 phosphonium cations, alkylated diazabicyclo-[5,4,0]-
16 undec-7-ene and related cations, or any other cation
17 that gives rise to compounds termed ionic liquids.
18 The anion for the process is preferably one that is
19 stable to chemical alteration during the reaction
20 and imparts desirable physical characteristics to
21 the ionic liquid. Some suitable anions for the
22 ionic liquid are bis-trifluoromethanesulfonimide,
23 bis-pentafluoroethanesulfonimide,
24 hexafluorophosphate(V), tetrafluoroborate(III),
25 trifluoromethanesulfonate, cyanamide, fluoro or
26 perfluoroalkylsulfonate, halide, sulfate,
27 hydrogensulfate, alkylsulfate, alkylsulfonate,
28 arylsulfate, arylsulfonate, nitrate, carboxylate,
29 phosphate, hydrogenphosphate, dihydrogenphosphate,
30 alkylphosphate, alkylphosphonate, phosphonate,

1 nitrite, arsenate, antimonate, haloaluminate,
 2 aluminate, borate, silcate, haloindate(III),
 3 gallate, alkylborate, halogallate or any other anion
 4 that gives rise to an ionic liquid.
 5 Examples of ionic liquids are given below:
 6



7
8

9 Preferably the ionic liquid or the catalyst or the
 10 ionic liquid and catalyst combination is insoluble
 11 in low- or non-polar organic solvents such as
 12 diethyl ether or hexane.

13

14 In addition to ionic liquids being excellent media
 15 for the execution of the Friedel-Crafts and other
 16 reactions, a second major benefit of this invention
 17 is that the catalyst and ionic liquid can be
 18 recycled and reused in many reactions. This means
 19 that catalysts are not lost. This is an improvement
 20 over reactions performed in nitromethane, which is
 21 an explosive solvent and is hard to recycle.

22

1 The chemical reactions of the present invention may
2 be carried out at temperatures between temperatures
3 of from -100 °C to 450 °C. Preferably the reaction
4 is performed at a temperature between 20 °C and the
5 boiling point of the reactants.

6

7 The present invention further provides a process
8 whereby the bis-triflimide catalyst or related
9 fluoroalkylsulfonated compound may be generated *in*
10 *situ* by the addition of a metal or a metal compound
11 (for example, a metal halide) to a bis-triflimide
12 salt (or other bis-triflimide compound) or related
13 fluoroalkylsulfonated compound. This process can
14 be carried out in the absence of a solvent or in an
15 ionic liquid. An example of this would be the
16 addition of a metal salt to a bis-triflimide ionic
17 liquid (or hydrogen bis-triflimide to an ionic
18 liquid) to generate a catalyst that is capable of
19 catalysing the desired chemical reaction. This can
20 be achieved by taking a metal or metal compound, not
21 necessarily a bis-triflimide salt (for example a
22 metal halide such as, ZnCl₂ or SnCl₄), and dissolving
23 (reacting) it in a bis-triflimide ionic liquid or
24 other source of bis-triflimide (for example,
25 HN(SO₂CF₃)₂). A suitable source of bis-triflimide
26 ions is [emim][NTf₂]. To this combination, the
27 reactants, e.g. alkylating, acylating or sulfonating
28 agent and aromatic compound can be added, with
29 heating if necessary. The products can be separated
30 from the catalyst at the end of the reaction by

1 distillation or solvent extraction with a solvent in
2 which, for example, the catalyst and ionic liquid
3 combination are insoluble (for example,
4 cyclohexane).

5

6 After the reaction of the present invention, the
7 catalyst may be separated from the
8 products/remaining reactants. Preferably the
9 separation process does not destroy the catalyst.
10 When the products of the reactions are aryl ketones,
11 alkyl-aromatic compound, or sulfones, these are
12 usually readily separated from the catalyst or ionic
13 liquid/catalyst mixture by several different means
14 as these are generally neutral covalent molecules.
15 These are usually (but not necessarily) neutral
16 covalent molecules, which are. The simplest and
17 preferred means is vacuum distillation (typically at
18 1 mm Hg) of the product and by-product directly from
19 the reaction vessel (Kugelrohr distillation is
20 preferred but not essential). The catalyst and ionic
21 liquid, having no measurable vapour pressure, remain
22 in the reaction vessel. The catalyst and/or ionic
23 liquid can be immediately reused upon cooling. A
24 second valuable method for the separation of the
25 ionic liquid/catalyst from the products is solvent
26 extraction. The ionic liquid and catalyst are
27 insoluble in low or non-polar organic solvents or
28 supercritical fluids. The reaction vessel can be
29 washed with a solvent or mixture of solvents such
30 that the product and by-product dissolve in the

1 solvent, whereas the ionic liquid and catalyst
2 remain in a separate solution. The separation can
3 be effected by decantation or other means. Suitable
4 solvents for this separation are alkanes
5 (cyclohexane, hexane, petroleum ether or other
6 alkanes or alkane-like compounds), aromatics
7 (toluene, benzene, xylene or other compounds
8 containing an aromatic group), ethers (such as
9 diethyl ether, dibutyl ether) or esters (such as
10 ethyl acetate, amyl acetate), supercritical
11 solvents, or any other material capable of allowing
12 for the separation of the catalyst (and ionic liquid
13 if present) from the products or reagents. Another
14 method involved azeotropic separation with compounds
15 such as steam (for example steam distillation).
16 Some halogenated solvents such as dichloromethane or
17 chloroform partially dissolve the ionic liquid and
18 catalyst and are therefore of lesser use in this
19 process. Thus the present invention provides a
20 process where the product is easily separated from
21 the catalyst or catalyst/ionic liquid combination or
22 solvent containing combination by solvent
23 extraction, distillation, vacuum distillation, steam
24 distillation, pervaporation, azeotropic
25 distillation, precipitation, crystallisation, phase
26 separation, supercritical fluid extraction or any
27 other non-destructive physical process. The present
28 invention further provides a process where the
29 product is easily separated from the catalyst or
30 catalyst / ionic liquid combination or solvent

1 containing combination by solvent extraction using
2 one or more of the following methods: (a) with
3 alkanes or boiling alkanes (eg. cyclohexane at 80
4 °C), (b) vacuum distillation at pressures preferably
5 between 0.01 mmHg and 10 mmHg, (c) steam
6 distillation or with the use of superheated steam at
7 temperatures up to 500 °C, (d) phase separation, (e)
8 supercritical fluid extraction preferably with
9 carbon dioxide.

10

11 The present invention relates to the use of metal
12 bis-triflimides in solvent-free conditions or in
13 ionic liquids. The reactions of aromatics both more
14 and less reactive than anisole can be achieved in
15 this invention, as well as the reaction of anisole
16 itself. The present invention also provides a
17 method of generating the catalyst *in situ* thus
18 obviating the need to isolate the metal bis-
19 triflimide catalyst and simplifying the experimental
20 procedure. One of the principal benefits of this
21 invention is that the product(s) of the reaction can
22 be easily separated from the catalyst and/or ionic
23 liquid - catalyst combination by a physical process
24 such as distillation, steam stripping or by solvent
25 extraction with an inert solvent (including
26 supercritical fluids) or molecular solvents. The
27 ionic liquid and/or the catalyst (which usually
28 remains in the ionic liquid during the separation
29 process) can be reused for further reactions.
30 Further reactants can simply be added to the ionic

1 liquid and/or the catalyst once the previous
2 products/reactants have been removed.

3

4 The present invention is illustrated by the
5 following figures and examples.

6

7 Figure 1 shows the variation of yield with time in
8 the metal bis-triflimide catalysed reaction of
9 benzoyl chloride with toluene.

10

11 Figure 2 shows the variation of yield with time in
12 the 1% FeCl₃ and 1% Fe bis-triflimide catalysed
13 reaction of benzoyl chloride with toluene in
14 [bmim] [NTf₂].

15

16 Figure 3 shows the variation of yield with time in
17 the synthesis of phenyl-4-chlorophenyl sulfone.

18

19 Figure 4 shows the variation of yield with time for
20 five reaction catalysed by 1 mol% metal chlorides
21 dissolved in [bmim] [NTf₂] for the reaction of
22 toluene with benzoyl chloride to give methyl
23 benzophenone at 110°C.

24

25 **Example 1:** The reaction of toluene with benzoyl
26 chloride with cobalt(II) bis-triflimide catalyst.

27

28 Cobalt(II) bis-triflimide (0.13 g, 0.21 mmol) was
29 added to toluene (3.0g, 32.5 mmol) and benzoyl
30 chloride (3.0 g, 21.3 mmol) in a 25 cm³ round

1 bottomed flask equipped with a magnetic stirrer and
2 reflux condenser. The mixture was heated under
3 reflux for 3 hours (judged to be at least 99 %
4 complete by gas chromatographic analysis), and
5 cooled to room temperature. Petroleum ether (15
6 cm³, bp = 40-60 °C) was added and the catalyst
7 precipitated out of solution. The solution of the
8 product was decanted and the flask washed with a
9 further 15 cm³ of petroleum ether. The solvent was
10 evaporated from the combined petroleum ether
11 extracts and the product purified by vacuum
12 distillation (bp = 160-170 °C @ 1 mmHg) in a
13 Kugelrohr apparatus.. This gave methylbenzophenone
14 (4.05 g, 97 % isolated yield). The catalyst can be
15 reused immediately by adding toluene and benzoyl
16 chloride to the flask (containing the precipitate)
17 and repeating the reaction.

18

19 **Example 2:** The reaction of toluene with benzoyl
20 chloride with cobalt(II) bis-triflimide catalyst in
21 [emim][NTf₂].

22

23 Cobalt(II) bis-triflimide (0.13 g, 0.21 mmol) was
24 added to 1-ethyl-3-methylimidazolium bis-
25 trifluoromethanesulfonimide ([emim][NTf₂]) (2.0 g)
26 in a 25 cm³ round-bottomed flask equipped with a
27 magnetic stirrer and reflux condenser, and the
28 mixture stirred until the catalyst dissolved.
29 Toluene (3.0g, 32.5 mmol) and benzoyl chloride (3.0
30 g, 21.3 mmol) were added. The mixture was heated

1 under reflux for 0.5 hours (judged to be at least 99
2 % complete by gas chromatographic analysis), and
3 cooled to room temperature. Petroleum ether (15
4 cm³, bp = 40-60°C) was added and the catalyst and
5 ionic liquid formed a separate phase. The solution
6 of the product was decanted and the flask
7 (containing the ionic liquid and catalyst) washed
8 three times with 15 cm³ of petroleum ether. The
9 solvent was evaporated from the combined petroleum
10 ether extracts and the product purified by vacuum
11 distillation (bp = 160-170 °C @ 1 mmHg) in a
12 Kugelrohr apparatus. This gave methylbenzophenone
13 (4.02 g, 96 %). The catalyst and ionic liquid
14 combination can be reused immediately by adding
15 toluene and benzoyl chloride to the flask and
16 repeating the reaction, without loss of activity.

17
18 Examples 1 and 2 show that the acylation of toluene
19 with benzoyl chloride can be carried out with a
20 cobalt(II) bis-triflimide catalyst and that this can
21 be performed with or without an ionic liquid
22 present. However, with the ionic liquid, faster
23 reaction rates are obtained and the catalyst can be
24 recycled more easily. Without the ionic liquid, the
25 products of this reaction are obtained in
26 quantitative yield using 1 mol % catalyst after 3
27 hours heating under reflux (example 1). The
28 reaction time is reduced to 30 minutes when the
29 reaction is carried out in the ionic liquid

1 [emim] [NTf₂] ([emim] = 1-ethyl-3-methylimidazolium)
2 (example 2).

3

4 Example 3: The reaction of toluene with benzoyl
5 chloride with nickel(II) bis-triflimide catalyst in
6 [emim] [NTf₂].

7

8 Nickel(II) bis-triflimide (0.13 g, 0.21 mmol) was
9 added to 1-ethyl-3-methylimidazolium bis-
10 trifluoromethanesulfonimide ([emim] [NTf₂]) (2.0 g)
11 25 cm³ in a round-bottomed flask equipped with a
12 magnetic stirrer and reflux condenser, and the
13 mixture stirred until the catalyst dissolved.
14 Toluene (3.0g, 32.5 mmol) and benzoyl chloride (3.0
15 g, 21.3 mmol) were added. The mixture was heated
16 under reflux for 1 hour (judged to be at least 99 %
17 complete by gas chromatographic analysis), and
18 cooled to room temperature. Petroleum ether (15
19 cm³, bp = 40-60°C) was added and the catalyst and
20 ionic liquid formed a separate phase. The solution
21 of the product was decanted and the flask
22 (containing the ionic liquid and catalyst) washed
23 three times with 15 cm³ of petroleum ether. The
24 solvent was evaporated from the combined petroleum
25 ether extracts and the product purified by vacuum
26 distillation (bp = 160-170 °C @ 1 mmHg) in a
27 Kugelrohr apparatus. This gave methylbenzophenone
28 (4.04 g, 97 % isolated yield). The catalyst and
29 ionic liquid combination can be reused immediately
30 by adding toluene and benzoyl chloride to the flask

1 and repeating the reaction, without loss of
2 activity.

3

4 The results from Examples 2 and 3 are shown in
5 Table.

6

7 **Table 1,** The gas chromatographic (GC) yields of
8 benzophenones derived from the reaction of benzoyl
9 chloride with toluene with 1% metal bis-triflimide
10 catalyst in [emim] [NTf₂].

Compound	Yield	Time / h
Co(NTf ₂) ₂	99	0.5
Ni(NTf ₂) ₂	99	1

11

12 **Example 4**

13 Anisole (0.30 cm³, 2.8 mmol), acetic anhydride (0.50
14 cm³, 5.0 mmol), M(NTf₂)_n catalyst (0.1375 mmol (M =
15 Al, n=3; M = Zn, n = 2; M = Yb, n = 3; M = Y, n =
16 3)) were dissolved in the ionic liquid [bmim][PF₆].
17 These four reactions were heated at 30 °C for 24
18 hours. The course of the reaction was determined by
19 HPLC analysis of the reaction mixture and the yields
20 are shown in Table 2.

21

22 **Table 2,** The variation of GC yield with time for
23 the acetylation of anisole with acetic anhydride
24 with metal bis-triflimide catalysts in [bmim][PF₆].

25

26

27

Catalyst	% Yield (35 min)	% Yield (115 min)	% Yield (245 min)	% Yield (1375 min)
Al(NTf ₂) ₃	45	55	61	63
Zn(NTf ₂) ₃	23	36	44	61
Yb(NTf ₂) ₃	49	61	64	69
Y(NTf ₂) ₃	55	62		71

1

2 **Example 5**

3 Anisole (0.50 cm³, 4.6 mmol), benzoic anhydride
 4 (1.15 g, 5.06 mmol), M(NTf₂)_n catalyst (0.23 mmol (M
 5 = Al, n=3, 0.20 g; M = Ce, n = 4, 0.29 g)) were
 6 dissolved in the ionic liquid [bmim][NTf₂] (2.0 g).
 7 These two reactions were heated at 60 °C for 24
 8 hours. The course of the reaction was determined by
 9 gas chromatographic analysis of the reaction mixture
 10 and the yields are shown in Table 3.

11

12 **Table 3,** The variation of GC yield with time for
 13 the benzoylation of anisole with benzoic anhydride
 14 with metal bis-triflimide catalysts in [bmim][PF₆].

15

Catalyst	% Yield (60 min)	% Yield (120 min)	% Yield (180 min)	% Yield (1350 min)
Al(NTf ₂) ₃	44	62	67	68
Ce(NTf ₂) ₄	32	49	56	84

16

17 **Example 6**

18 Fluorobenzene (5.77 g, 60 mmol), 4-fluorobenzoyl
 19 chloride (4.75 g, 30 mmol), ZnCl₂ (1.36 g, 10 mmol)
 20 and [emim][NTf₂] were placed in an autoclave and
 21 heated with stirring for 48 hours at 160 °C. The

1 reactor was cooled and the pressure (HCl gas)
2 released. Gas chromatographic analysis showed that
3 a 99 % conversion to a mixture of 2,4'-
4 difluorobenzophenone, 3,4'-difluorobenzophenone,
5 4,4'-difluorobenzophenone in 17 : 8 : 75 ratio
6 respectively. The difluorobenzophenones were
7 isolated by solvent extraction with petroleum ether
8 (bp = 40 - 60 °C), followed by evaporation of the
9 solvent. The ionic liquid / zinc chloride catalyst
10 system could be used in further reactions, with
11 similar activity. This result shows that the
12 classically unreactive aromatic compound
13 fluorobenzene can be acylated with 4-fluorobenzoyl
14 chloride to give isomers of 2-, 3-, or 4-4'-
15 difluorobenzophenone in [emim][NTf₂] using an *in*
16 *situ* zinc catalyst. This catalyst was generated by
17 dissolving zinc(II) chloride in the [emim][NTf₂]
18 ionic liquid. The reaction gave a 95 % yield (17 :
19 8 : 75 *o*-, *m*-, *p*- isomer ratio).

20

21 **Example 7**

22 Benzoic acid (0.31 g, 2.5 mmol), *m*-xylene (0.53 g,
23 5.0 mmol), [bmim][NTf₂] (0.50 g) and M(NTf₂)₂ (M = Co
24 (0.14 g, 0.25 mmol), or Zn (0.15 g, 0.25 mmol) were
25 placed in flasks equipped with stirrers and
26 condensers. The contents of the flask were heated
27 under reflux (ca 140 - 150 °C) for 2 days, then
28 cooled to room temperature. The products were
29 analysed by gas chromatographic analysis and found
30 to give 93 and 87 % conversions (for Co and Zn bis-

1 triflimide reactions respectively) to 2,4-
2 dimethylbenzophenone and, it is believed to be, 2,6-
3 dimethylbenzophenone (11 : 1 isomer ratio in both
4 cases). The results show that Zinc and cobalt bis-
5 triflimide have been found to catalyse the
6 benzylation of *m*-xylene with benzoic acid. The
7 reaction is slower than the corresponding reaction
8 with benzoyl chloride. The catalyst was recycled and
9 the reaction was repeated. The results of the
10 repeat experiment are shown in Table 4.

11

12 **Table 4**, The yields of benzophenones derived from the
13 reaction of benzoic acid with *m*-xylene with 10%
14 recycled metal bis-triflimide catalyst in
15 [bmim] [NTf₂] at 140 °C for 48 hours.

Compound	% Yield	2,4- to 2,6- ratio
Zn(NTf ₂) ₂	40	11 : 1
Co(NTf ₂) ₂	82	11 : 1

16

17 These are remarkable results given the low
18 reactivity of benzoic acid. It is to be noted that
19 this reaction produces water as a byproduct and as
20 such it is a very environmentally friendly reaction.
21 Furthermore, it utilises a non corrosive starting
22 material (benzoic acid) and therefore is a safer
23 reaction to perform than the corresponding reaction
24 with benzoyl chloride. It can be concluded that
25 this is a superior way to produce
26 dimethylbenzophenone.

27

1 **Example 8:** The reaction of toluene with benzoyl
2 chloride with zinc(II) or copper(II) bis-triflimide
3 catalyst in [emim] [NTf₂].

4

5 Copper or zinc (II) bis-triflimide (0.13 g, 0.21
6 mmol) was added to a mixture of toluene (3.0g, 32.5
7 mmol) and benzoyl chloride (3.0 g, 21.3 mmol). The
8 mixture was heated under reflux for 72 hours (the
9 reaction was monitored by gas chromatographic
10 analysis, by taking a drop of the reaction mixture
11 and suspending it in petroleum ether (b.p. = 40-
12 60°C) and filtering off the catalyst. The starting
13 materials and products, which are soluble in the
14 petroleum ether extract, were cooled to room
15 temperature. Petroleum ether (15 cm³, bp = 40-60°C)
16 was added and the catalyst and formed a separate
17 phase. The solution of the product was decanted and
18 the flask (containing the catalyst) washed three
19 times with 15 cm³ of petroleum ether. The solvent
20 was evaporated from the combined petroleum ether
21 extracts and the product purified by vacuum
22 distillation (bp = 160-170 °C @ 1 mmHg) in a
23 Kugelrohr apparatus. This gave methylbenzophenone
24 (4.0 g, 95 %). The catalyst can be reused
25 immediately by adding toluene and benzoyl chloride
26 to the flask and repeating the reaction, without
27 loss of activity. The yields as determined by gas
28 chromatographic analysis are shown in Table 5.

29

1 **Table 5**, the yields of benzophenones derived from the
 2 reaction of benzoyl chloride with toluene with 1 %
 3 copper(II) or 1 % zinc(II) bis-triflimide catalysts.
 4 The figure in brackets refers to the *o*-, *m*- and *p*-
 5 isomer ratios.

Time / h	Yield with Zn(NTf ₂) ₂	Yield with Cu(NTf ₂) ₂
24	83	52
48	99 (22 : 1 : 77)	
72		99 (20 : 2 : 78)

6.
 7 Zinc(II) and copper(II) bis-triflimide compounds were
 8 found to be effective acylation catalysts for the
 9 benzoylation of toluene.

10
 11 **Example 9:** The reaction of *o*-xylene with benzoyl
 12 chloride with an aluminium(III) bis-triflimide
 13 catalyst.

14
 15 Aluminium (III) bis-triflimide (0.10 g) was added to
 16 a mixture of *o*-xylene (3.0g, 28.2 mmol) and benzoyl
 17 chloride (3.0 g, 21.3 mmol). The mixture was heated
 18 at 120 °C for 18 hours (the reaction was monitored
 19 by gas chromatographic analysis, by taking a drop of
 20 the reaction mixture and suspending it in petroleum
 21 ether (b.p. = 40-60°C) and filtering off the
 22 catalyst. The starting materials and product are
 23 soluble in the petroleum ether extract), and cooled
 24 to room temperature. Petroleum ether (15 cm³) was
 25 added and the catalyst and formed a separate phase.

1 The yields as determined by gas chromatographic
2 analysis was 99% with a 6.0 : 1 3,4- to 2,3-
3 dimethylbenzophenone isomer ratio. Aluminium(III)
4 bis-triflimide was found to be an effective catalyst
5 for the benzoylation of o-xylene. The reaction gave
6 a quantitative yield of two isomers of the
7 corresponding benzophenone (6 : 1 3,4- to 2,3-
8 isomer ratio) after 18 h at 120 °C, using 1 mol % of
9 catalyst.

10

11 **Example 10:** The reaction of toluene with benzoyl
12 chloride with metal bis-triflimide catalyst.

13

14 Various metal (1-ethyl-3-methylimidazolium, Li, Mg,
15 Ca, Mn, Co, Ni, Cu, Zn, Sn, Pb, Al) bis-triflimide
16 salts (1 mol %) was added to a mixture of toluene
17 (3.0g, 32.6 mmol) and benzoyl chloride (3.0 g, 21.3
18 mmol). The mixture was heated at 110 °C for up to
19 120 hours. The reaction was monitored at regular
20 intervals by gas chromatographic analysis and the
21 reaction stopped when the reaction was judged to be
22 99 % complete by cooling to room temperature.
23 Petroleum ether (15 cm³) was added and the catalyst
24 and formed a separate phase. The product was
25 isolated be decanting the petroleum ether extract,
26 followed by Kugenrohr distillation at 1 mm Hg. The
27 yields after various time intervals are given in
28 Table 6. The product formed is methylbenzophenone.
29 In all these reactions, the isomer ratio was found to
30 be approximately 76 % para and 24 % ortho. This

1 results are shown in Table 6. Table 1 lists the
 2 times required for Co and Ni bis-triflimide in
 3 [emim] [NTf₂].

4

5 **Table 6,** The yields of benzophenones derived from the
 6 reaction of benzoyl chloride with toluene with 1%
 7 metal bis-triflimide catalyst.

Compound	Yield / %	Time / h
[emim] [NTf ₂]	< 1	48
Li NTf ₂	< 5	120
Mg (NTf ₂) ₂	99	48
Ca (NTf ₂) ₂	< 5	120
Mn (NTf ₂) ₂	99	5
Co (NTf ₂) ₂	99	3
Ni (NTf ₂) ₂	99	4
Cu (NTf ₂) ₂	99	72
Zn (NTf ₂) ₂	99	48
Sn (NTf ₂) ₂	55	48
Pb (NTf ₂) ₂	95	6
Al (NTf ₂) ₃	99	24

8

9 From Table 6, a remarkable difference in reactivity
 10 between the compounds chosen is observed. Of these,
 11 four compounds appear to have unexpectedly high
 12 reactivity, namely those of manganese, cobalt,
 13 nickel and lead, whereas compounds such as zinc bis-
 14 triflimide and aluminium bis-triflimide have
 15 relatively modest activity. This is completely
 16 different to "conventional Friedel-Crafts chemistry"
 17 which would suggest that the Al bistriflimide should

1 be the best catalyst. Of particular remark is the
2 catalytic reactivity of Co and Pb. Lithium and
3 calcium bis-triflimide in contrast show very poor
4 activity and with [emim] [bis-triflimide], little or
5 no reaction was observed.

6

7 **Example 11:** The reaction of chlorobenzene with
8 benzoyl chloride with nickel(II) bis-triflimide
9 catalyst in [bmim][NTf₂].

10

11 Nickel(II) bis-triflimide (0.062 g, 0.1 mmol) was
12 added to 1-butyl-3-methylimidazolium bis-
13 trifluoromethanesulfonimide ([bmim][NTf₂]) (1.0 g)
14 in a 25 cm³ round-bottomed flask equipped with a
15 magnetic stirrer and reflux condenser, and the
16 mixture stirred until the catalyst dissolved.
17 Chlorobenzene (1.68 g, 15 mmol) and benzoyl chloride
18 (1.41 g, 10 mmol) were added. The mixture was
19 heated under reflux for 72 hours and was analysed by
20 gas chromatographic analysis as in previous
21 examples. The reaction was cooled to room
22 temperature. Petroleum ether (15 cm³, bp = 40-60 °C)
23 was added and the catalyst and ionic liquid formed a
24 separate phase from the petroleum ether layer. The
25 solution of the product (in petroleum ether) was
26 decanted and the flask (containing the ionic liquid
27 and catalyst) washed three times with 15 cm³ of
28 petroleum ether. Concentration of the organic
29 extract, followed by Kugelrohr distillation at 1 mm
30 Hg (bp = 170-190 °C), gave chlorobenzophenone (1.65

1 g, 74 %). GC analysis showed 78 % yield after 72 hours, with a 70 : 8 4- to 2- isomer ratio. This is a remarkable result, as chlorobenzene is known to be classically unreactive in acylation reactions. It has not previously been possible to isolate significant quantities of the products of the acylation of chlorobenzene.

8
9 **Example 12:** The reaction of chlorobenzene with
10 benzoyl chloride with cobalt(II) bis-triflimide or
11 zinc(II) bis-triflimide catalyst in [bmim][NTf₂].

12
13 In two separate reactions, either zinc(II) bis-
14 triflimide (0.16 g, 5 mol %) or cobalt(II) bis-
15 triflimide (0.15 g, 5 mol %) was added to 1-butyl-3-
16 methylimidazolium bis-trifluoromethanesulfonimide
17 ([bmim][NTf₂]) (1.0 g) 25 cm³ in a round-bottomed
18 flask equipped with a magnetic stirrer and reflux
19 condenser, and the mixture was heated gently and
20 stirred until the catalyst dissolved.
21 Chlorobenzene (0.68 g, 6 mmol) and benzoyl chloride
22 (0.72 g, 5 mmol) were added. The mixture was heated
23 under reflux for 18 hours and was analysed by gas
24 chromatographic analysis as in previous examples.
25 The reaction was cooled to room temperature.
26 Cyclohexane (15 cm³) was added and the catalyst and
27 ionic liquid formed a separate phase. The solution
28 of the product was decanted and the flask
29 (containing the ionic liquid and catalyst) washed
30 three times with 15 cm³ cyclohexane followed by

1 Kugelrohr distillation at 1 mm Hg (bp = 180-200 °C).
2 This gave a mixture of 2- and 4-chlorobenzophenone.
3 GC yield = 97 % (6.8 : 1 *p*- to *o*- isomer ratio) for
4 cobalt catalyst and 55 % GC yield (6.5 : 1 *p*- to *o*-
5 isomer ratio) for the zinc catalyst.

6

7 The reaction of chlorobenzene with benzoyl chloride
8 was investigated, as chlorobenzene is much more
9 difficult to acylate. Although reasonable yields
10 could be obtained with 1 mol % catalyst, it was
11 found that 5-mol % catalyst gave more acceptable
12 reaction rates. The reaction was found to be 95 %
13 complete with cobalt bis-triflimide after 18 hours
14 and 55 % complete with zinc bis-triflimide (Table
15 7). The catalyst was found to be less active after
16 extracting the product with boiling cyclohexane and
17 recycling the ionic liquid / catalyst. The activity
18 of the catalyst was restored by adding a trace of
19 hydrogen bis-triflimide (0.1 mol %).

20

21 **Table 7**, The yields of benzophenones derived from the
22 reaction of benzoyl chloride with chlorobenzene with
23 5% metal bis-triflimide catalyst in [bmim] [NTf₂].

Compound	Yield	Time / h
Co(NTf ₂) ₂	95	18
Zn(NTf ₂) ₂	55	18

24

25 **Example 13:** The reaction of toluene with benzoyl
26 chloride with hydrogen and metal bis-triflimide
27 catalyst.

1
2 Various metal bis-triflimide compounds: Sr(II),
3 Ba(II), In(III), In(III) in [bmim][NTf₂], Cr(III),
4 Ce(IV), Yb(III), and hydrogen bis-triflimide
5 {HN(SO₂CF₃)₂} (1 mol %) were added to a mixture of
6 toluene (1.38 g, 15.0 mmol) and benzoyl chloride
7 (1.41 g, 10.0 mmol). The mixture was heated at 110
8 °C for up to 120 hours. The reaction was monitored
9 at various intervals by gas chromatographic analysis
10 and the reaction stopped after 5 days. The yields
11 of methylbenzophenone with respect to time are shown
12 in Figure 1. The reaction of benzoyl chloride and
13 toluene gave 2- and 4-methylbenzophenone. All these
14 compounds were found to be active Friedel-Crafts
15 catalysts, but with considerably different
16 activities. Of these, the activities of indium(III)
17 and iron(III) (Example 14) are the most notable, as
18 they are exceptionally good catalysts. The p- to o-
19 selectivities were in the range 3.9 to 4.4 to 1,
20 with the indium and iron catalysts giving 4.4 : 1
21 selectivity.

22
23 **Example 14:** The reaction of toluene with benzoyl
24 chloride with iron(III) bis-triflimide or iron(III)
25 chloride dissolved in [bmim][NTf₂].

26
27 In two separate reactions, either iron(III) bis-
28 triflimide (1 mol %) or iron(III) chloride (1 mol %)
29 was added to 1-butyl-3-methylimidazolium bis-
30 trifluoromethanesulfonimide ([bmim][NTf₂]) (1.0 g)

1 25 cm³ in a round-bottomed flask equipped with a
2 magnetic stirrer and reflux condenser, and the
3 mixture was heated gently and stirred until the
4 catalyst dissolved. Toluene (1.38 g, 15 mmol) and
5 benzoyl chloride (1.41 g, 10 mmol) were added. The
6 mixture was heated under reflux for 48 hours and was
7 analysed by gas chromatographic analysis as in
8 previous examples. The yield of methylbenzophenone
9 with respect to time is shown in Figure 2. Here,
10 the activity of the iron catalyst was tested in two
11 separate ways: (a) with 1% FeO(NTf₂) in [bmim][NTf₂]
12 and (b) 1% FeCl₃ in [bmim][NTf₂]. In both cases, the
13 activity and selectivity were similar, indicating
14 that FeCl₃ and FeO(NTf₂) are possibly precursors to
15 catalyst, when dissolved in excess [bmim][NTf₂].

16
17 Example 15: The reaction of toluene with methane
18 sulfonyl chloride with zinc(II) bis-triflimide.
19

20 Zinc(II) bis-triflimide (0.13 g, 2.5 mol %) was
21 added to a round-bottomed flask equipped with a
22 magnetic stirrer and reflux condenser. Toluene
23 (1.38 g, 15 mmol) and methane sulfonyl chloride
24 (1.14 g, 10 mmol) were added. The mixture was
25 heated under reflux for 24 hours and was analysed by
26 gas chromatographic analysis as in previous
27 examples. All the methane sulfonyl chloride had
28 reacted and three isomers of (2-, 3- and 4-
29 methylphenyl)methylsulfone had formed (yield = 99
30 %), isomer ratio = 35 : 18 : 47 for the o-, m- and

1 *p*- isomers. The product was extracted from the
2 catalyst by dissolving it in cyclohexane (20 cm³)
3 followed by decantation of the cyclohexane extract.
4 The catalyst was washed with cyclohexane (2 x 20
5 cm³) and the combined cyclohexane extracts were
6 concentrated on a rotary evaporator. The product
7 was Kugelrohr distilled at 100-110°C to give 1.62 g
8 of a colourless oil (96 % isolated yield).

9

10 **Example 16:** The reaction of benzene with benzene
11 sulfonyl chloride with zinc(II) bis-triflimide.

12

13 Zinc(II) bis-triflimide (0.062 g, 1 mol %) was
14 dissolved in [bmim][NTf₂] (1.0 g) in a round-
15 bottomed flask equipped with a magnetic stirrer and
16 reflux condenser. Benzene (1.56 g, 20 mmol) and
17 benzene sulfonyl chloride (1.76 g, 10 mmol) were
18 added. The mixture was heated under reflux for 18
19 hours and was analysed by gas chromatographic
20 analysis as in previous examples. All the benzene
21 sulfonyl chloride had reacted diphenyl sulfone had
22 formed (yield = 99 %). The product was extracted
23 from the catalyst and ionic liquid by dissolving it
24 in boiling cyclohexane (5 x 30 cm³) followed by
25 decantation of the cyclohexane extract. The
26 diphenylsulfone crystallised on cooling and was
27 collected by filtration (2.03 g, 93 % isolated
28 yield). The reaction of benzene with benzene
29 sulfonyl chloride gave the expected diphenyl sulfone
30 in 99% yield with a Zn(NTf₂)₂ catalyst (18 h at

1 reflux). The diphenyl sulfone was extracted with
2 boiling cyclohexane and the ionic liquid and
3 catalyst could be reused.

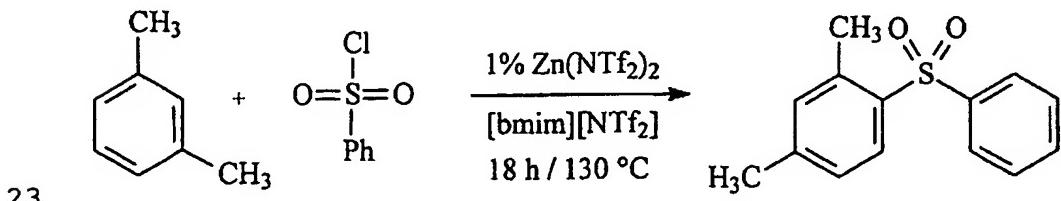
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5 **Example 17:** The reaction of *m*-xylene with benzene
6 sulfonyl chloride with zinc(II) bis-triflimide.

7

8 Zinc(II) bis-triflimide (0.062 g, 1 mol %) was
9 dissolved in [bmim][NTf₂] (1.0 g) in a round-
10 bottomed flask equipped with a magnetic stirrer and
11 reflux condenser and *m*-xylene (2.12 g, 20 mmol) and
12 benzene sulfonyl chloride (1.76 g, 10 mmol) were
13 added. The mixture was heated under reflux for 18
14 hours and was analysed by gas chromatographic
15 analysis as in previous examples. All the benzene
16 sulfonyl chloride had reacted and mostly 2,4-
17 dimethyldiphenylsulfone had formed (yield = 99 %, 20
18 : 1 isomer ratio {by NMR}). The major product is
19 shown below, the structure of the minor isomer is
20 not known but is believed to be the 2,6-dimethyl
21 isomer.

22



The product was extracted from the catalyst and
ionic liquid by dissolving it in boiling cyclohexane
(5 x 30 cm³) followed by decantation of the

1 cyclohexane extract. The 2,4-
2 dimethyldiphenylsulfone crystallised on cooling and
3 was collected by filtration.

4

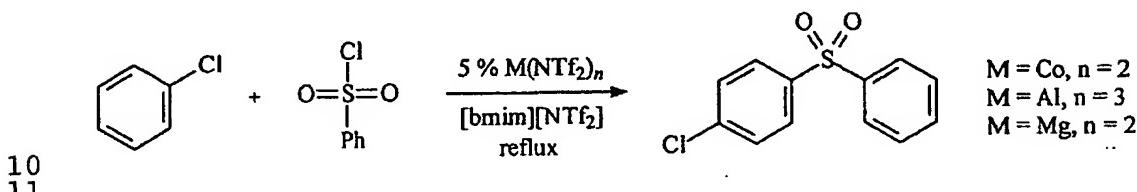
5 **Example 18:** The reaction of chlorobenzene with
6 benzene sulfonyl chloride with metal bis-triflimide
7 catalysts.

8

9 In three separate reactions, either magnesium(II)
10 bis-triflimide (0.058 g, 0.1 mol), aluminium(III)
11 bis-triflimide (0.87 g, 0.1 mmol) or cobalt(II) bis-
12 triflimide (0.062 g, 0.1 mmol) was dissolved in
13 [bmim][NTf₂] (0.5 g) in a round-bottomed flask
14 equipped with a magnetic stirrer and reflux
15 condenser. Chlorobenzene (1.68 g, 15 mmol) and
16 benzene sulfonyl chloride (1.76 g, 10 mmol) were
17 added. The mixture was heated under reflux for 144
18 hours and monitored by gas chromatographic analysis
19 as in previous examples. The yields with respect to
20 time are given in Figure 3. The product was
21 extracted from the catalyst and ionic liquid by
22 dissolving it in boiling cyclohexane (4 x 10 cm³)
23 followed by decantation of the cyclohexane extract.
24 The 2- and 4-chlorodiphenylsulfone (9:1 *p*- to *o*-
25 isomer ratio) crystallised on cooling and was
26 collected by filtration. The selectivity was 9:1 for
27 the *p*- isomer and the *o*- isomer was the minor isomer
28 in all cases. Coincidentally, the reaction of benzoyl
29 chloride with chlorobenzene also gave the same
30 selectivity and similar reaction rates. Phenyl-4-

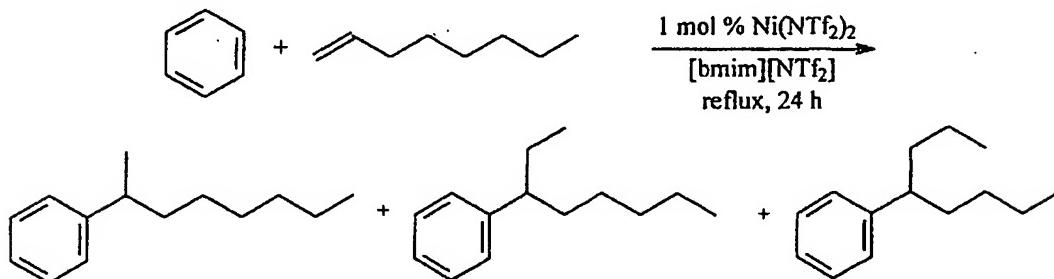
1 chlorophenylsulfone is an insecticide. The reaction
 2 was found to be slow using 1 mol % catalyst, but 5
 3 mol % catalyst gave acceptable reaction rates. The
 4 metal salts chosen were aluminium(III), cobalt(II)
 5 and magnesium(II) bis-triflimide, in the ionic
 6 liquid [bmim][NTf₂]. All three catalysts were found
 7 to be effective for this reaction. The reaction is
 8 shown below.

9



1 liquid and catalyst were prepared for reuse by
2 heating at 60 °C under vacuum for 1 hour. The ionic
3 liquid and catalyst were used for further reactions
4 of benzene with oct-1-ene without loss of activity.
5 This is an alkylation of benzene with an alkene
6 using a metal bis-triflimide catalyst. Benzene and
7 oct-1-ene react in the presence of 1% nickel(II)
8 bis-triflimide in [bmim][NTf₂] to form three isomers
9 of octyl benzene and a small amount of hexadecene
10 (unknown isomeric distribution). This reaction
11 shown below:

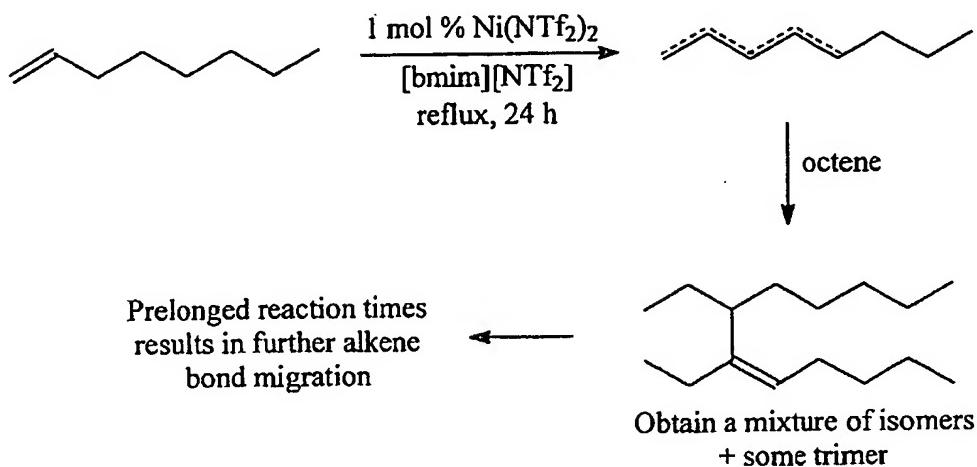
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14 The alkylation of benzene with oct-1-ene.
15 The reaction gave a 70 % yield (by GC) of three
16 isomers of octylbenzene. The isomer ratio was
17 determined to be 0.75 : 1.00 : 2.03, with the 4-
18 phenyloctene as the major product and 2-phenyloctene
19 as the minor product. During the course of the
20 reaction, isomerisation of oct-1-ene to a number of
21 isomers of octene was observed, and the rate of this
22 isomerisation process was considerably faster than
23 the alkylation reaction. It was found that the ionic
24 liquid / catalyst combination remained active on a

1 second run. To confirm that the minor product of
 2 the reaction was an octene dimer, the same reaction
 3 was performed, but without any benzene present
 4 (shown below).

5



6

7 The dimerisation of oct-1-ene.

8

9 The reaction proceeded initially with isomerisation
 10 of octene to a mixture of 4 isomers of octene.
 11 After 18 hours, the reaction was almost complete (>
 12 95 % conversion). The products were a large number
 13 of isomers of dimerised and trimerised octene. As
 14 the reaction was left to run for 6 days, a
 15 broadening of the cluster of GC peaked for the dimer
 16 and trimer was observed, indicating that further
 17 isomerisation was occurring.

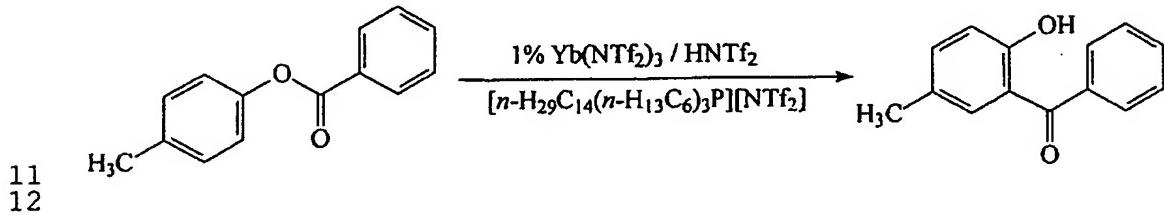
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19 Example 20: The dimerisation of oct-1-ene with
 20 nickel(II) bis-triflimide.

1
2 Nickel(II) bis-triflimide (0.062 g, 0.1 mmol) was
3 dissolved in [bmim][NTf₂] (0.5 g) in a round-
4 bottomed flask equipped with a magnetic stirrer and
5 reflux condenser. Oct-1-ene (1.12 g, 10 mmol) was
6 added. The mixture was heated under reflux for 18
7 hours and was analysed by gas chromatographic
8 analysis as in previous examples. The oct-1-ene peak
9 disappeared and three isomers of octene (oct-2-ene,
10 oct-3-ene and oct-4-ene) were formed. Hydrogen bis-
11 triflimide was added (0.0028 g, 0.1 mmol) and the
12 mixture was heated for a further 18 hours. Gas
13 chromatographic analysis showed that the reaction
14 was almost complete (> 99%), and gave a mixture of
15 isomers of hexadecene and tetracosene (trimer of
16 octene). The less dense product phase was decanted
17 from the ionic / catalyst phase and purified by
18 Kugelrohr distillation at 1 mm Hg. The ionic liquid
19 and catalyst were prepared for reuse by heating at
20 60 °C under vacuum for 1 hour. The ionic liquid and
21 catalyst were used for further dimerisation
22 reactions of oct-1-ene without loss of activity.
23
24 **Example 21:** The Fries rearrangement of 4-
25 methylphenoxybenzoate with hydrogen and metal bis-
26 triflimide compounds.
27
28 Ytterbium(III) bis-triflimide (0.1 g) and hydrogen
29 bis-triflimide (0.01 g) was dissolved in [n-H₂₉C₁₄(n-
30 H₁₃C₆)₃P][NTf₂] (1.0 g) in a round-bottomed flask

1 equipped with a magnetic stirrer and reflux
 2 condenser. 4-methylphenoxybenzoate (1.0 g) was
 3 added. The mixture was heated under reflux for 24
 4 hours at 60 °C and was analysed by gas
 5 chromatographic analysis as in previous examples.
 6 The product of the reaction was 2-hydroxy-5-
 7 methylbenzophenone (90 % yield). The isomerisation
 8 of 4-methylphenoxybenzoate to 2-hydroxy-5-
 9 methylbenzophenone is shown below.

10



1 examples. The cyclohexene peak disappeared and
2 peak(s) due to alkylation of the aromatic compound
3 and peaks due to dimerisation reactions of
4 cyclohexene were formed (see Example 26 for
5 details). The ionic liquid and catalyst were
6 prepared for reuse by heating at 60 °C under vacuum
7 for 1 hour. The ionic liquid and catalyst were used
8 for further reactions of benzene with cyclohexene
9 without loss of activity.

10

11 **Example 23:** The reaction of benzene with dodec-1-ene
12 with metal bis-triflimides, triflates and hydrogen
13 bis-triflimide.

14

15 In ten separate reaction vessels (a multi-cell glass
16 reactor with stirrers and condensers) metal
17 triflimide or metal triflate compounds (see Table
18 below) were added together with hydrogen bis-
19 triflimide (0.01 g) to $[n\text{-H}_{29}\text{C}_{14}(n\text{-H}_{13}\text{C}_6)_3\text{P}][\text{NTf}_2]$ (2.0
20 g) and stirred until the metal compound had
21 dissolved. Benzene (3.8 g, 50 mmol) and dodec-1-
22 ene (0.84 g, 5.0 mmol) were added. The mixtures
23 were heated at 80 °C for 24 hours. The excess
24 benzene was distilled off. The mixture was analysed
25 by NMR upon cooling to room temperature. The ionic
26 liquid and catalyst were prepared for reuse by
27 heating at 60 °C under vacuum for 1 hour. The ionic
28 liquid and catalyst were used for further reactions
29 of benzene with dodec-1-ene without loss of
30 activity. The results are shown in Table 8 below.

1 **Table 8**

Compound	Mass / g	Unreacted dodecene	Isomerised dodecene	Dodecyl benzene
Yb(NTf ₂) ₃	1.02	0	0	100
Co(NTf ₂) ₂	0.62	0	99	1
Cu(NTf ₂) ₂	0.62	0	1	99
Pb(NTf ₂) ₂	0.76	0	100	0
In(NTf ₂) ₃	0.95	0	0	100
Ga(NTf ₂) ₃	0.63	0	61	39
Zn(OTf ₂) ₂	0.36	67	33	0
Cu(OTf ₂) ₂	0.36	1	96	3
Yb(OTf ₂) ₃	0.53	0	91	9
La(OTf ₂) ₃	0.59	0	60	40

2

3 **Example 24:** The reaction of toluene with benzoyl
 4 chloride with metal compounds dissolved in
 5 [bmim][NTf₂].

6

7 In five separate reactions, either titanium(IV)
 8 chloride (1 mol %) or tin(IV) chloride (1 mol %), or
 9 tungsten(VI) chloride, or hafnium(IV) chloride or
 10 palladium(II) chloride was added to 1-butyl-3-
 11 methylimidazolium bis-trifluoromethanesulfonimide
 12 ([bmim][NTf₂]) (2.0 g) 25 cm³ in a round-bottomed
 13 flask equipped with a magnetic stirrer and reflux
 14 condenser, and the toluene (2.81 g, 30 mmol) and
 15 benzoyl chloride (2.84 g, 20 mmol) were added. The
 16 mixtures was heated under reflux for 24 hours and
 17 was analysed by gas chromatographic analysis as in
 18 previous examples. The conversion of starting

1 materials to methylbenzophenone was quantitative
2 except for the palladium(II) catalysed reaction (75
3 % yield). The variation of yield with time in the
4 reaction of several new metal bis-triflimide salts
5 in the reaction of benzoyl chloride with toluene is
6 given in Figure 4. These reactions were performed
7 in parallel, and the yields were determined by GC
8 analysis.

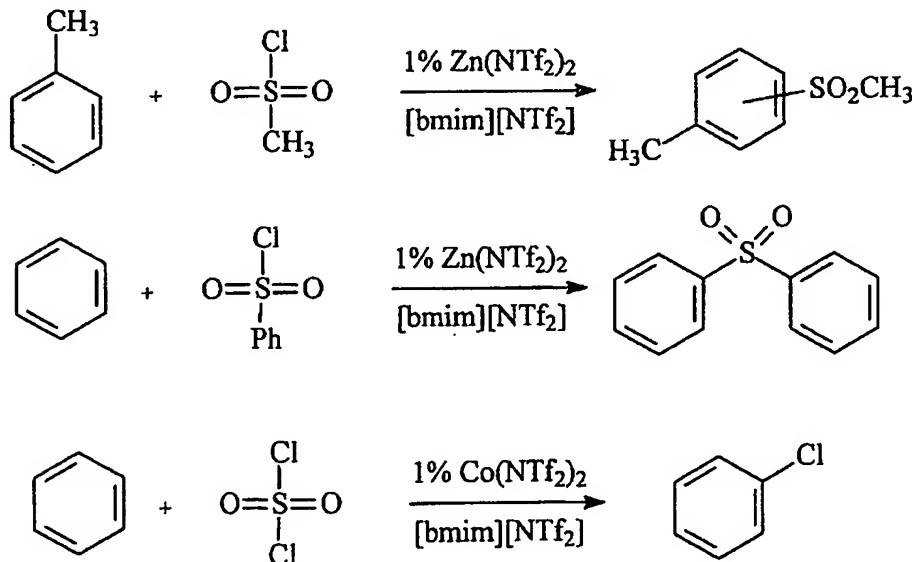
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10 In this invention, the use of a metal halide
11 dissolved in a bis-triflimide ionic liquid can be
12 used for reactions such as the Friedel-Crafts
13 reactions. This is useful where a particular metal
14 bis-triflimide salt is difficult to prepare or
15 isolate. In this invention, five metal halides
16 (chlorides) (1 mol % with respect to the reactants)
17 were dissolved in [bmim][NTf₂]. This combination
18 was used to catalyse the reaction of toluene with
19 benzoyl chloride to give methylbenzophenone. The
20 yield with respect to time is given in Figure 4.
21 All of the metals chosen gave the expected products
22 in good yield, but the combination of 1% mol tin(IV)
23 chloride in [bmim][NTf₂] was a particularly
24 effective catalyst. This process of using metal
25 compounds dissolved in an ionic liquid (usually bis-
26 triflimide) can also be used with compounds of other
27 metals (particularly transition metals (d-block) or
28 f-block metals)) not listed in Figures 3 or 4.

29

30 **Example 25**

1 A number of aromatic sulfonylation reactions were
 2 performed. These reactions are very similar to
 3 Friedel-Crafts acylation reactions and are performed
 4 under similar conditions. The key difference is
 5 that a $-SO_2-X$ group replaces a $-CO-X$ (X = leaving
 6 group). In most cases, the selectivities,
 7 reactivities and yields were found similar to the
 8 corresponding acylation reaction. The reaction of
 9 sulfonyl chloride with benzene resulted in the
 10 formation of chlorobenzene (quantitatively) and SO_2 .
 11 This is as is found in many other reactions of SO_2Cl_2
 12 with aromatic compounds performed in molecular
 13 solvents.

14



15

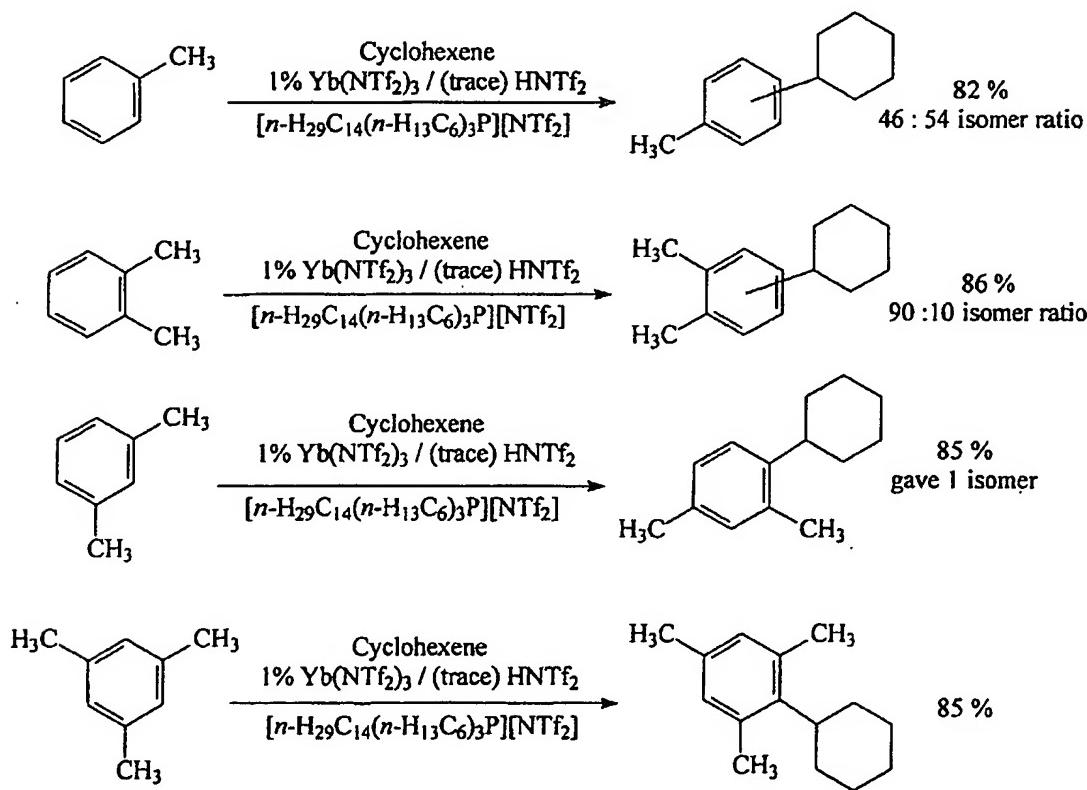
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17 **Example 26**

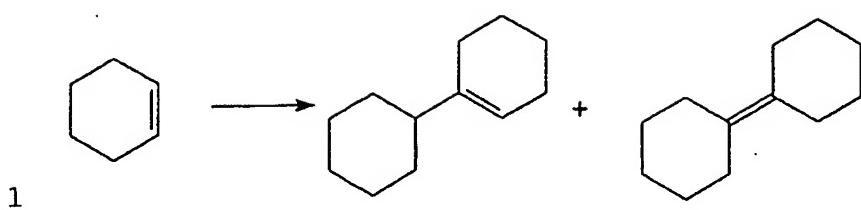
18 The alkylation of various aromatic compounds with
 19 cyclohexene in a phosphonium ionic liquid with 10 %
 20 ytterbium(III) bis-triflimide with a trace of

hydrogen bis-triflimide were carried out. A side reaction also takes place that results in the formation of a dimer of cyclohexene (see below) and this results in a slight reduction in the yield of the Friedel-Crafts reaction. However, it should be noted that this demonstrates that metal triflimide compounds can be used for dimerisation and oligomerisation reactions.

9

10
11

The reaction of aromatics with cyclohexene in a phosphonium ionic liquid for 12 hours at 80 °C is shown above. Below is shown the dimerisation of cyclohexene.



1 **CLAIMS**

2

3 1. A process for carrying out a chemical reaction
4 which is catalysed by one or more metal or hydrogen
5 fluoroalkylsulfonylated compound which process
6 comprises carrying out said reaction in the presence of
7 an ionic liquid or in solvent-free conditions.

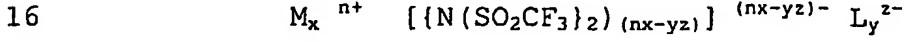
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9 2. A process as claimed in claim 1 wherein the one or
10 more metal or hydrogen fluoroalkylsulfonylated compound
11 is a metal or hydrogen bistriflimide compound.

12

13 3. A process according to claim 2 wherein the
14 bistriflimide compound has the following formula:

15



17

18 where M is hydrogen or a metal;
19 L is a negative or neutral ligand;
20 n is 2,3,4,5,6,7 or 8;
21 x is greater than or equal to 1;
22 y is 0,1,2,3,4,5,6,7 or 8; and
23 z is 0, 1,2,3 or 4.

24

25 4. A process according to any one of the preceding
26 claims wherein M is a metal selected from the metals in
27 groups 1 to 16 and the lanthanides and the actinides.

28

29 5. A process according to any one of the preceding
30 claims wherein the chemical reaction is one of :
31 (a) an electrophilic substitution reaction, or

1 (b) an isomerisation, polymerisation or
2 rearrangement of a chemical compound or
3 molecule.

4 6. A process according to claim 5 wherein the
5 chemical reaction is a reaction between an aromatic
6 compound and an alkylating, acylating or sulfonating
7 agent.

8

9 7. A process according to claim 5 wherein the
10 chemical reaction is a rearrangement of esters of
11 phenols to acyl phenols.

12

13 8. A process according to any one of the preceding
14 claims which comprises carrying out said reaction in
15 solvent free conditions wherein the one or more metal
16 or hydrogen fluoroalkylsulfonylated compound is added
17 directly to the reactants.

18

19 9. A process according to any one of the preceding
20 claims which comprises carrying out the reaction in the
21 presence of an ionic liquid which comprises dissolving
22 or suspending the one or more metal or hydrogen
23 fluoroalkylsulfonylated compound in an ionic liquid.

24

25 10. A process according to claim 9 wherein the ionic
26 liquid comprises a cation chosen from 1-alkylpyridinium
27 or 1,3-dialkylimidazolium cation, alkyl- or poly-
28 alkylpyridinium, alkyl or poly-alkylimidazolium, alkyl
29 or poly-alkylpyrazolium, alkyl or poly-alkyl ammonium,
30 alkyl or poly-alkyl phosphonium and alkylated

1 diazabicyclo-[5,4,0]-undec-7-ene; and an anion chosen
2 from bis-trifluoromethanesulfonimide,
3 bis-pentafluoroethanesulfonimide,
4 hexafluorophosphate(V), tetrafluoroborate(III),
5 trifluoromethanesulfonate, cyanamide, fluoro or
6 perfluoroalkylsulfonate, halide, sulfate,
7 hydrogensulfate, alkylsulfate, alkylsulfonate,
8 arylsulfate, arylsulfonate, nitrate, carboxylate,
9 phosphate, hydrogenphosphate, dihydrogenphosphate,
10 alkylphosphate, alkylphosphonate, phosphonate, nitrite,
11 arsenate, antimonate, haloaluminate, aluminate, borate,
12 silicate, haloindate(III), gallate, alkylborate and
13 halogallate.

14

15 11. A process according to any one of the preceding
16 claims wherein the catalyst or the catalyst and ionic
17 liquid combination are subsequently separated from the
18 reaction mixture.

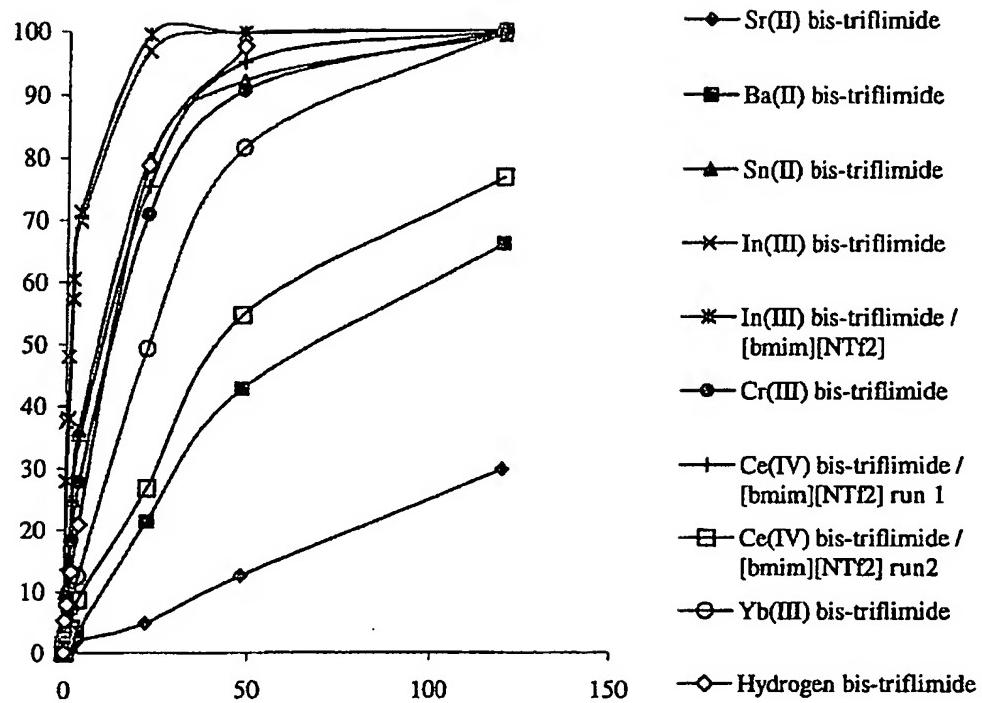
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20 12. A process according to claim 11 wherein the
21 catalyst or the catalyst and ionic liquid combination
22 are subsequently recycled.

23

1 **Figure 1**

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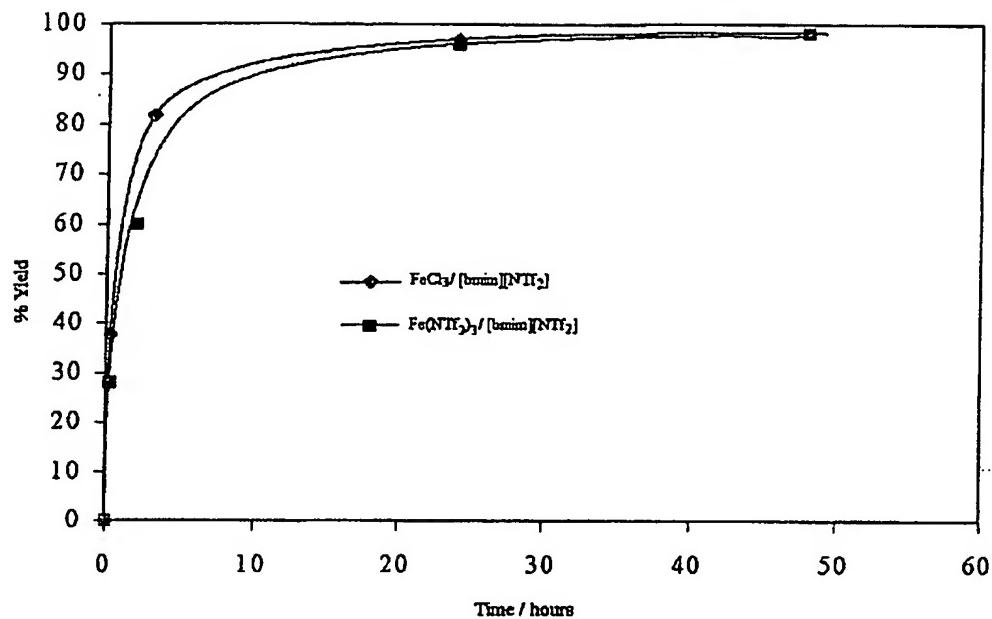
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11

1 **Figure 2**

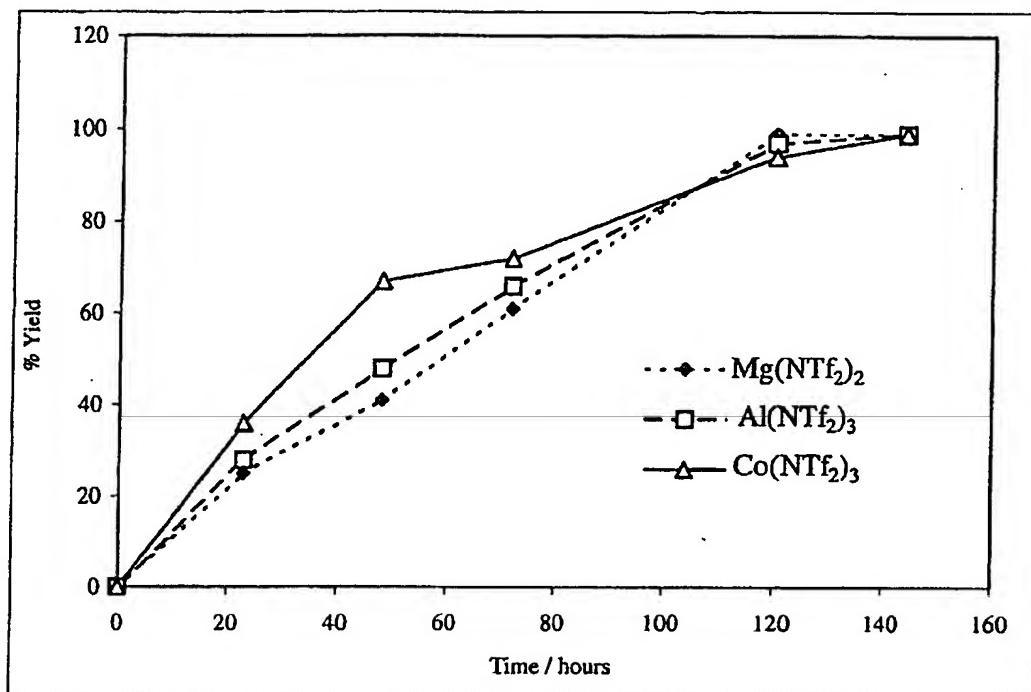
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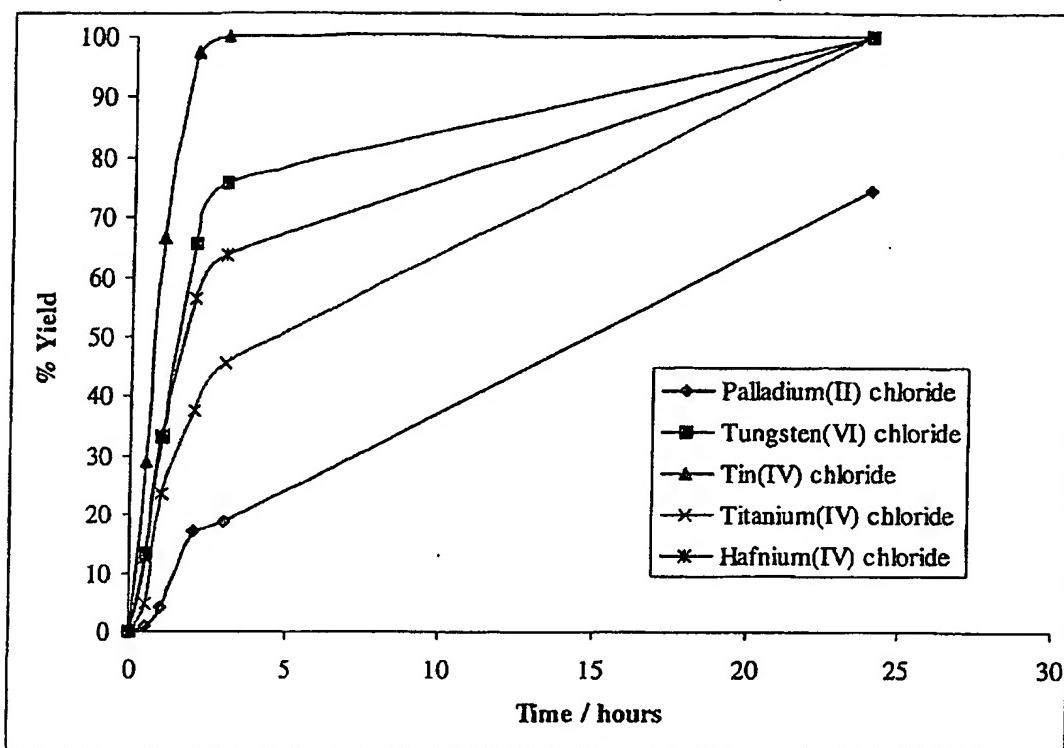
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1 Figure 3



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1 Figure 4



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